



Headspace sorptive extraction for the detection of combustion accelerants in fire debris



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ABSTRACT

A novel method for separation and identification of ignitable liquid residues in fire debris by gas chromatography and mass spectrometry is presented. Preconcentration of the analytes was carried out using the simple headspace sorptive extraction (HSSE) technique. Polydimethylsiloxane stir bars were used as the enrichment phase, and parameters affecting both the adsorption and desorption stages were carefully optimized. Extraction was carried out at 50 °C for 1 h. Stir bars were desorbed thermally in the GC injection port, thus avoiding the use of organic solvents. The results for five ignitable liquids, including gasoline and diesel fuel, using HSSE were compared with those obtained with a solid-phase microextraction method, with HSSE appearing as a more sensitive alternative.

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1. Introduction

The destructive nature of fire makes it difficult to obtain criminal evidence from the fire scene. In many cases, the chance of identifying the arsonist is related with the possibility of collecting, analyzing and tracking any combustion accelerant that may have been used to encourage the fire. The special relevance of such evidence has led to the development of various techniques for the analysis of fire debris that enable investigators to establish whether or not a fire was started intentionally with a high degree of sensitivity and reliability. The main contribution of these analytical techniques has been to qualitatively identify some compounds, whose presence in the fire debris may indicate that some kind of combustion accelerant was used to start the fire. Although a wide range of products can be used as combustion accelerants, the most common are gasoline, diesel, kerosene and turpentine [1]. Information about the type of accelerant used in arson may help investigators track down the suspected arsonist.

Gas chromatography (GC) is the most used analytical technique for the analysis of accelerants in fire debris. Ignitable liquids are composed primarily of hydrocarbons, and so a universal detector has to be coupled to GC. Flame ionization detection (FID) has

traditionally been used for this purpose, but its use has been declining due to the identification capabilities of mass spectrometry (MS) [2–4]. In fact, the American Society for Testing and Materials (ASTM) has made MS the standard method for the investigation of fire debris [5]. On the other hand, the modalities of two-dimensional GC [6] and tandem mass spectrometry [7] have been proposed to remove interferences originated by fire debris pyrolysates.

Different sample preparation techniques have been used for isolating ignitable liquid residues from fire debris [2,8,9]. Solvent extraction [10], which is a time consuming technique [11], has been substituted in most applications by passive headspace concentration, because of its simplicity and the lower level of interference provided. Passive headspace concentration has been carried out with activated charcoal strips (ACS) [12–15]. Passive adsorbents other than ACS and which can be thermally desorbed due to their thermal stability have also been checked [16,17]. Of note is the Radiello passive commercial sampler which also uses activated carbon as adsorbent and CS₂ for desorption [18]. Solid-phase microextraction (SPME) overcomes the inherent disadvantages of very long adsorption times as well as the use of toxic organic solvents required when ACS is used, such as CS₂, dichloromethane or pentane [19–24]. SPME has been recommended as the ASTM standard for fire debris analysis as a screening test [25]. On the other hand, a polymer particle-packed needle device has been presented for the concentration of ignitable liquids

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as an interesting alternative to SPME [26]. Also, in order to increase the extraction efficiency of compounds with high boiling points, dynamic headspace extraction has been presented [27,28]. A miniaturized liquid-liquid microextraction (LLME) technique has also been applied in headspace mode for fire debris analysis [29], using benzyl alcohol as the extraction phase.

Even though SPME has proved to be a rapid and highly sensitive preconcentration technique that allows the detection of combustion accelerants even at trace levels, it has some major drawbacks, such as the low robustness of the fibers, their limited useful life, their cost and their low capacity which results in higher displacement rate. Headspace sorptive extraction (HSSE) is a microextraction technique derived from the application of stir bar sorptive extraction (SBSE) in headspace mode [30]. In this technique, a 1 or 2 cm stir bar coated with a thick film of 0.5 or 1 mm of polydimethylsiloxane (PDMS), meaning a total volume between 24 μL and 126 μL of PDMS, is hung in the headspace of a vial containing the sample. The heating of this vial, led to the evaporation of the analytes to the headspace, from where they are absorbed into the stir bar coating, which acts as extraction phase. Once equilibrium between phases is reached, the stir bar is removed from the vial and submitted to desorption prior to GC analysis. The introduction of the retained compounds into the GC system is accomplished by a thermal desorption in a specific injector, comprising a thermal desorption unit (TDU) and a programmed temperature vaporizing (PTV) injector. This preconcentration technique provides higher recoveries and so higher sensitivity than SPME, due to the larger amount of extracting phase involved (24–126 μL versus 0.5 μL). In addition, the robustness of the stir bar assembly facilitates its application, reaching useful life about 100 cycles in headspace mode.

Despite the advantages of HSSE over SPME, to the best of our knowledge, it has not been previously applied for the preconcentration of combustion accelerants in fire debris. The present work proposes an HSSE–TD–GC–MS procedure for the detection of ignitable liquid residues in fire debris.

2. Material and methods

2.1. Instrumentation

Commercial stir bars (20 mm length) coated with a 0.5 mm layer of PDMS (48 μL) were obtained from Gerstel (Mullheim an der Ruhr, Germany), and were conditioned in an empty thermal desorption tube at 275 °C for 0.5 h with helium at a flow desorption rate of 50 mL min^{−1} prior to their use. Inserts for Twister[®] headspace vials were tried (Gerstel). The sample introduction system into the gas chromatograph was composed of a thermal desorption unit (TDU-2) equipped with an autosampler (MPS-2) and a programmed temperature vaporization (PTV) cooled injector system (CIS-4) provided by Gerstel. The experimental conditions used for the sample introduction system are summarized in Table 1.

GC analyses were performed on an Agilent 6890 N (Waldbronn, Germany) gas chromatograph equipped with a 30 m \times 0.25 mm \times 0.25 μm VF-23MS (50% diphenyl–50% dimethylpolysiloxane) capillary column. The oven temperature program and other chromatographic conditions are summarized in Table 1. An Agilent 5973 quadrupole mass selective spectrometer equipped with an inert ion source was employed for detection purposes, working under scan mode in the 40–400 m/z range. Identification of the compounds was confirmed by spectra comparison with a mass spectra library.

All analyses were performed in 15 mL clear glass vials. To prevent analyte evaporation, the vials were sealed with hole-caps and PTFE-silicone septa were used. Laboratory-made systems,

Table 1

Experimental conditions of the TD–GC–MS procedure.

| | |
|------------------------------|------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Thermal desorption unit | |
| Mode | Splitless |
| Temperature program | 50–240 °C at 380 °C min ^{−1} , held 10 min |
| Desorption flow and pressure | 50 mL min ^{−1} , 7 psi |
| Cooled injector system | |
| Mode | Solvent venting |
| Liner | Tenax, 1 mm i.d. |
| Temperature program | 15–300 °C (5 min) at 650 °C min ^{−1} |
| GC–MS | |
| Capillary column | VF-23MS, 50% diphenyl-50% dimethylpolysiloxane 30 m \times 0.25 mm, 0.25 μm |
| Carrier gas | Helium (1 mL min ^{−1}) |
| Oven program | 40 °C held 8 min 40–90 °C at 25 °C min ^{−1} 90–120 °C at 30 °C min ^{−1} 120–150 °C at 15 °C min ^{−1} 150–200 °C at 10 °C min ^{−1} , held 2 min |
| Transfer line temperature | 280 °C |
| Quadrupole temperature | 150 °C |
| Ion source temperature | 230 °C |
| Ionization | Electron-impact mode (70 eV) |

consisting of a drilled block provided with an electronic temperature control system, were used for controlling the temperature during the sample extraction step.

2.2. Samples and analytical procedure

Different combustion accelerants, representing three of the eight main classes of the ASTM E 1618-06 ignitable liquid classification, including gasoline, diesel fuel (petroleum distillate), fire starter or barbecue lighter (BBQ), industrial solvent and turpentine (others–miscellaneous) were purchased from local stores. Working solutions (0.1% v/v) of these accelerants were prepared by dilution with methanol.

Soil and sawdust samples obtained from a local garden and a local shop, respectively, were used as debris simulants. Spiked samples were prepared by adding different volumes of the working solutions, in the range 10–100 μL , to 1 g of sample previously placed in glass vials.

Real fire debris of different accelerants were obtained by burning a sawdust–soil mixture (roughly 1:1) spiked with the undiluted accelerant and ignited by a propane torch in the open air, which was allowed to burn until mostly charred. About 1 g of the debris was placed in the extraction vessel (15 mL glass vials) for the HSSE procedure. A homemade magnetic holder was used to expose the PDMS stir bar to the vial headspace for 60 min at 50 °C (Fig. 1). Once extraction was accomplished, thermal desorption was carried out by placing the desorption tube in the TDU-2 connected to the PTV injector, and conducted to the GC–MS system.

For comparison purposes, a 100 μm PDMS SPME fibre was employed for accelerant preconcentration using previously reported extraction conditions and 240 °C and 2 min as desorption temperature and time, respectively.

3. Results and discussion

Preliminary experiments were carried out to optimize chromatographic separation using a mixture of the most widely used accelerants, gasoline and diesel, whose components include a wide number of analytes. In order to facilitate the rapid identification of the compounds, the oven program temperature selected provided

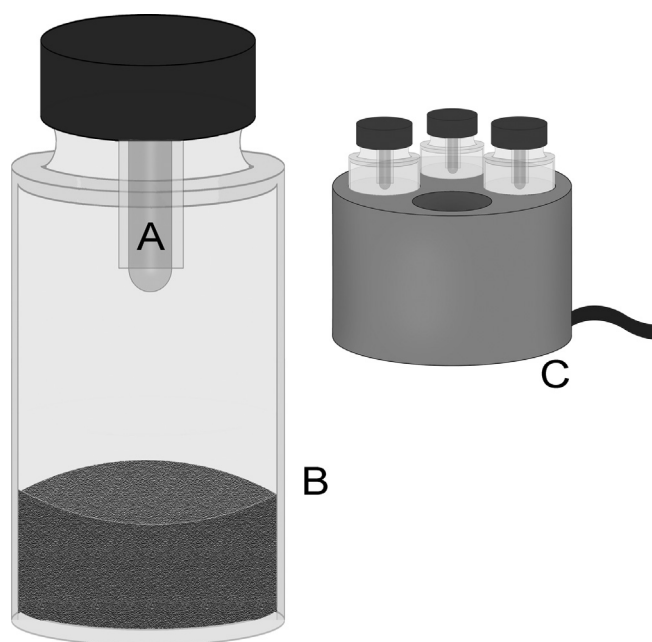


Fig. 1. Schematic diagram of the HSSE device: (A) HSSE stir bar, (B) sample vial and (C) heating block.

retention times in minutes for the *n*-alkanes close to the number of carbons, as can be seen in Table 2. Industrial solvent, BBQ lighter and turpentine, accelerants that are used to a lesser extent, were submitted to the selected oven program and the retention times for the main components of these accelerants appear in Table 2.

3.1. HSSE optimization

HSSE preconcentration involves two different and sequential stages: the extraction of analytes from the sample to the stir bar coating and their thermal desorption for injection into the GC. Different parameters, affecting both stages, were carefully studied. For this optimization process, the variations in the response obtained for eight compounds (mpXy, oXy, Cum, TMB, Dec, Und,

Dod and Tri, see Table 2), corresponding to the principal components of the most common fire accelerants (gasoline and diesel), were monitored. Considering the non-polar character of these compounds, polydimethylsiloxane (PDMS) was selected as the extracting phase.

Sampling temperature is one of the most important parameters in HSSE. High extraction temperatures favour the vaporization of the accelerant, shifting the equilibrium of the compounds studied to the headspace phase, from where they are extracted to the HSSE sorptive phase. However, excessively high temperatures may reduce the extraction efficiency. Five different temperatures, ranging from 25 to 75 °C were assayed, maintaining the extraction time at 1 h (see in Fig. 2A). Maximum response was achieved in all cases at 50 °C, which was selected as extraction temperature.

Variations in the vial volume alter the headspace:sample ratio, which can affect the extraction efficiency. Two different glass vial sizes, corresponding to 15 and 40 mL, were assayed. As shown in Fig. 2B, lighter compounds were more effectively extracted using 40 mL vials, while extraction of the heavier compounds was greater when 15 mL vials were used. Taking into account the lower sensitivity of these species, 15 mL vials were selected.

HSSE stir bars were exposed to the vial headspace using two different holders: commercial glass holders and homemade magnetic holders. The best results were obtained with the magnetic holders, especially in the case of heavier compounds. This can be explained by the fact that the PDMS stir bar coating is entirely exposed to the sample headspace when using the homemade holder, whereas commercial inserts are provided with a hole in the base, which is the only way for the sample headspace to come into contact with the coating phase.

The most important parameter affecting HSSE is commonly the extraction time, which was investigated from 0.5 to 3 h. HSSE extraction efficiency usually increases with extraction time, at least until equilibrium between sample, headspace and extracting phase is attained. As Fig. 3A shows, the equilibration time depends on the compound: lighter ones reach equilibrium in 0.5 h, while heavier species require longer extraction times. To ensure maximum sensitivity, an extraction time of 1 h was chosen.

Even though isothermal heating programs are usually used for extraction purposes, varying the temperature during the extraction step may increase extraction efficiency. Three different

Table 2
Main components in assayed combustion accelerants.

| Accelerant | Compound | RT, min | Monitored ions, <i>m/z</i> | LOD, ng g ⁻¹ |
|--------------------|------------------------------------|---------|----------------------------|-------------------------|
| Gasoline | Toluene | 5.6 | 51, 65, 91 | 0.2 |
| | <i>m</i> + <i>p</i> -Xylene (mpXy) | 9.4 | 77, 91, 105, 106 | |
| | <i>o</i> -Xylene (oXy) | 10.1 | 77, 91, 105, 106 | |
| | <i>n</i> -Propylbenzene | 10.7 | 77, 91, 105, 120 | |
| | Cumene (Cum) | 10.9 | 77, 91, 105, 120 | |
| | Trimethylbenzene (TMB) | 11.4 | 77, 91, 105, 120 | |
| Diesel fuel | Decane (Dec) | 9.9 | 43, 57, 71, 85, 99, 142 | 0.4 |
| | Undecane (Und) | 11.2 | 43, 57, 71, 85, 99, 156 | |
| | Dodecane (Dod) | 12.2 | 43, 57, 71, 85, 99, 170 | |
| | Tridecane (Tri) | 13.0 | 43, 57, 71, 85, 99, 184 | |
| | Tetradecane | 13.8 | 43, 57, 71, 85, 99, 198 | |
| | Pentadecane | 14.6 | 43, 57, 71, 85, 99, 212 | |
| Industrial solvent | Toluene | 5.6 | 51, 65, 91 | 0.1 |
| | Tetradecane | 13.8 | 43, 57, 71, 85, 99, 198 | |
| BBQ lighter | Tetradecane | 13.8 | 43, 57, 71, 85, 99, 198 | 0.4 |
| | Diethylphthalate | 18.2 | 149, 177 | |
| Trementine | Terpinene | 11.6 | 93, 136 | 0.7 |
| | Terpinolene | 12.0 | 93, 121, 136 | |
| | Tetramethylbenzene | 12.5 | 91, 115, 119, 134 | |
| | Cymene | 12.6 | 91, 119, 134 | |
| | Terpineol | 13.3 | 59, 93, 121, 134 | |

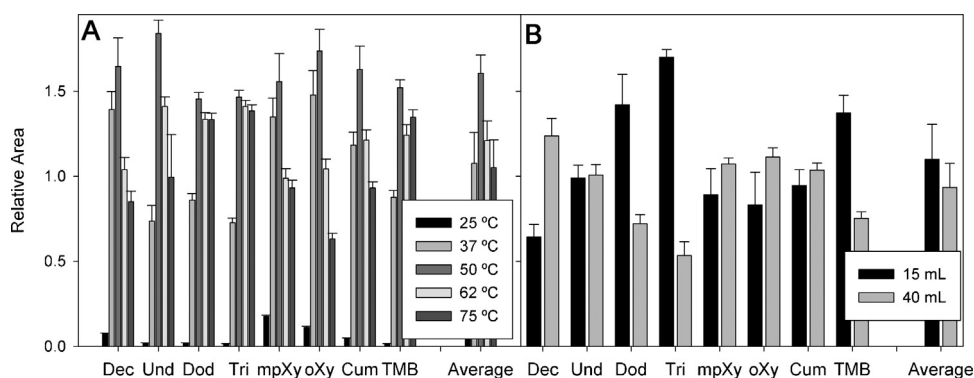


Fig. 2. Influence of extraction temperature (A) and vial volume (B) on the sensitivity of the analytes.

extraction temperature programs were tested: (a) an isothermal program at 50 °C for 1 h, (b) an increasing temperature program starting from 37 °C (held 15 min) and increased first to 50 °C (held 30 min) and then to 62 °C (held 15 min), and (c) a decreasing temperature program starting from 62 °C (held 15 min) and decreased first to 50 °C (held 30 min) and then to 37 °C (held 15 min). Three homemade heating blocks were set at 37, 50 and 62 °C, respectively, and the vials were transferred between them. As shown in Fig. 3B, a slightly higher response was obtained for several of the analytes using a decreasing temperature program. Nevertheless, taking into account that no significant advantages were found, the simplest isothermal heating program at 50 °C was finally adopted.

Desorption of the trapped analytes on the stir bar was carried out in a thermal desorption unit (TDU). In general, higher desorption temperatures and longer desorption times facilitate

the release of analytes from the extracting phase, but may reduce the useful life of the stir bar. Different desorption temperatures, ranging from 240 to 280 °C, the maximum recommended for the PDMS coating, were assayed. As shown in Fig. 4A, maximum response was attained at 240 °C, except for the heaviest compound (Tri), so 240 °C was selected. When different desorption times in the 5–10 min range were applied, the obtained signal increased with time (Fig. 4B), so 10 min was chosen.

A carrier gas is necessary to propel the analytes towards the PTV injector while they are being thermally desorbed in the TDU. Even though higher desorption flow rates usually increase the efficiency of the process, when different values between 50 and 100 mL min⁻¹ were assayed, maximum sensitivity was achieved at 50 mL min⁻¹ for all the compounds.

Desorbed compounds were focused in the PTV before entering the chromatographic column. Lower temperatures in this device

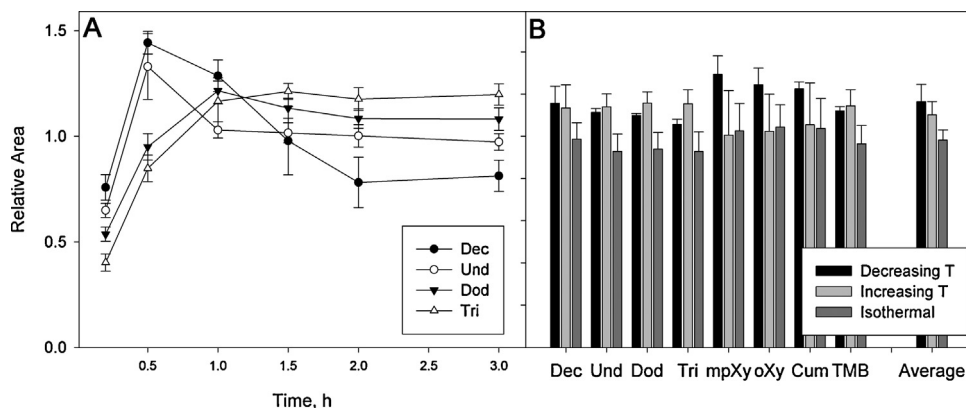


Fig. 3. Effect of the extraction time (A) and temperature program (B) on the analytical response of target compounds.

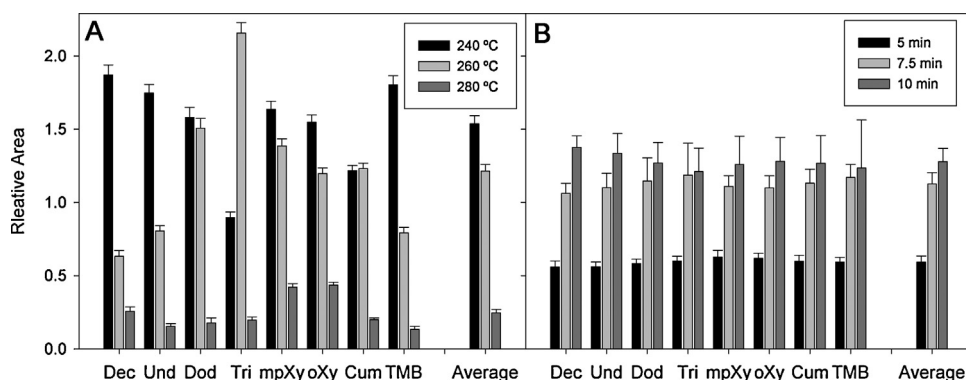


Fig. 4. Influence of the TDU desorption temperature (A) and time (B) on the sensitivity of the target compounds.

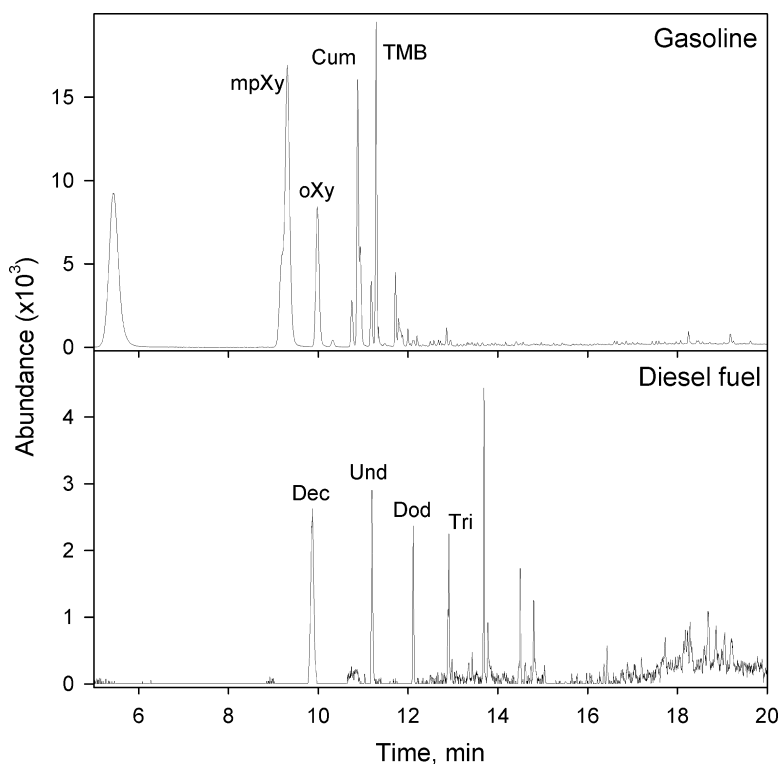


Fig. 5. HSSE-TD-GC-MS extracted ion chromatograms (according to Table 2) obtained for a sawdust sample spiked at 10 ng g⁻¹ concentration level with (A) gasoline and (B) diesel fuel.

mean lower losses and greater retention efficiency. Since the Peltier unit used only allows cooling to slightly below room temperature, 20 °C was selected as the focusing temperature.

Three different filling materials for the PTV liner were checked in order to facilitate the retention of the analytes: poly(2,6-diphenylphenylene oxide), fiberglass and PDMS. The liner filled with poly(2,6-diphenylphenylene oxide), an excellent retaining material for compounds containing from 5 to 26 carbon atoms, showed the best retention power for all the studied compounds, and provided good recoveries both for the more volatile and heavier ones. A PTV program temperature increasing from 205 to

300 °C at 10.5 °C s⁻¹, with a hold time of 5 min efficiently eluted the compounds retained in the liner into the chromatographic column.

3.2. Application to samples

Once the experimental conditions had been fixed, the proposed method was applied to the qualitative analysis of different combustion accelerants in spiked sawdust and soil samples. Fig. 5 shows the HSSE-TD-GC-MS elution profiles obtained for a sawdust sample spiked with the neat accelerant (gasoline or diesel

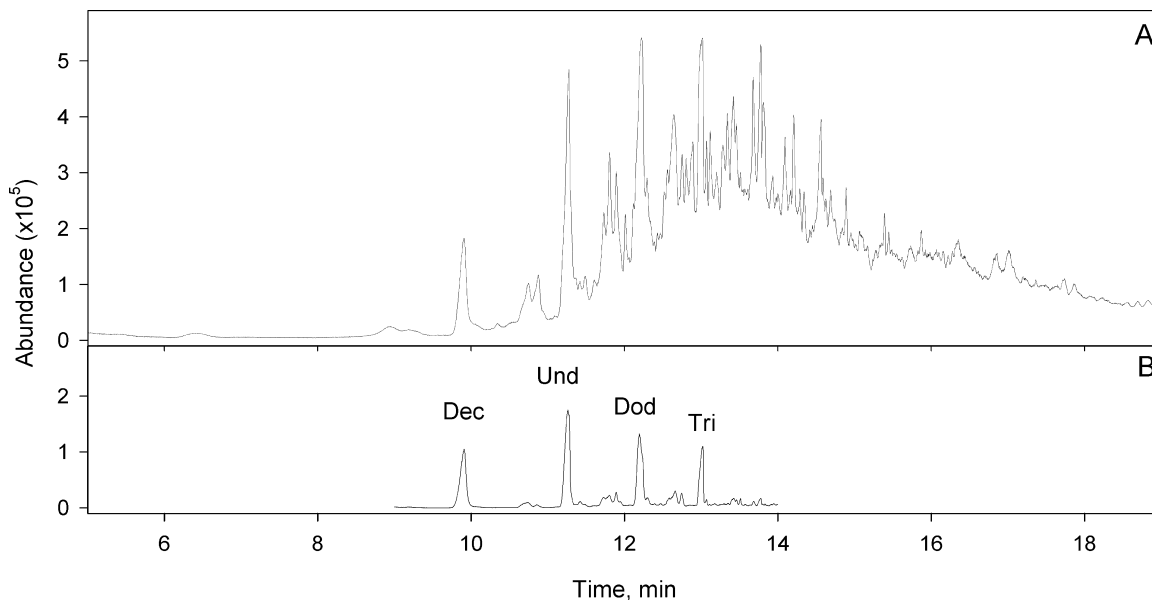


Fig. 6. Elution profile obtained from diesel fuel fire debris, showing the total ion (TIC) (A) and the extracted ion chromatograms (EIC) (according to Table 2) (B).

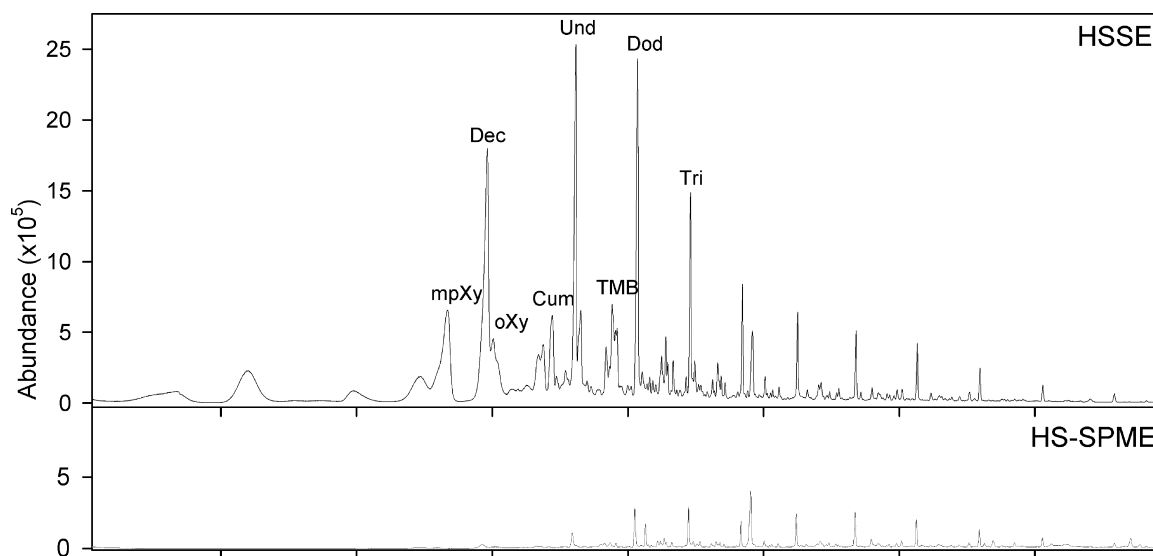


Fig. 7. Comparison of the elution profiles obtained for a soil sample spiked with a mixture of gasoline and diesel obtained using the proposed HSSE and a headspace SPME procedures.

fuel) at 10 ng g^{-1} . Each ignitable liquid was identified by its retention time as well as the main components in its mass spectrum (Table 2). Aromatic hydrocarbons were identified using their characteristic fragments of 77 and 91 m/z , while aliphatic hydrocarbons showed their major peaks at m/z 57 and 71. For confirmation purposes, full spectra comparison with a mass spectra library was performed.

Even though quantification does not usually form part of fire debris analysis, the sensitivity of the method, expressed as the smallest detectable amount of an accelerant that can be detected, was evaluated in terms of detection limit (LOD). LODs were calculated using the signal-to-noise ratio criterium, as the concentration that provides an analytical signal three times higher than the noise for the major component of each one of the five accelerants assayed. As shown in Table 2, the method provides LODs in spiked solid samples in the $0.1\text{--}0.7 \text{ ng g}^{-1}$ range, depending on the nature of the particular accelerant.

A real fire imposes such extreme conditions that most of the added combustion accelerants are burnt or evaporated. Therefore, in order to evaluate the performance of the proposed method in real conditions, real fire debris samples were prepared for every accelerant as previously described in Section 2.2. In spite of the complexity of the obtained chromatograms due to the pyrolysis products, the most relevant compounds of each accelerant could be easily identified using retention times as well as the extracted ion chromatograms of their main fragments. An example of this identification for a diesel fuel sample is shown in Fig. 6.

Two elution profiles obtained for the same gasoline and diesel spiked sample using the proposed HSSE procedure and SPME in the headspace mode, carried out in the experimental conditions stated in Section 2.2, are shown in Fig. 7. As expected, the higher PDMS extraction phase volume of the HSSE stir bar compared with the SPME fiber led to the more effective extraction of combustion accelerant compounds. Not only were the obtained signals higher using HSSE (from 20 to 100 fold depending on the compound), but also HSSE provided more detailed chromatograms, showing some compound peaks which were absent in the SPME chromatograms.

4. Conclusions

A HSSE-TD-GC-MS method for the detection of combustion accelerant compounds has been developed. The HSSE technique can easily be applied to the extraction of liquid accelerants from

fire debris, reducing the manipulation of the samples, as well as avoiding the use of solvents. Accelerants added to different materials could be extracted and detected with low detection limits. HSSE is proven to be a high sensitive preconcentration procedure for the detection of ignitable liquids in fire debris samples.

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